

Desorption of Diuron and Isoproturon from Undispersed Clay Loam Soil

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Abstract: Studies were conducted to investigate the desorption of diuron and isoproturon adsorbed on undispersed clay loam soil, and the influence of residence time in soil on desorption. The soil was treated at 0.6 or 3 mg kg⁻¹, at 70% moisture content and in the presence of sodium azide to prevent degradation. Measurement of herbicide concentrations in soil solution sampled by means of glass microfibre filters showed that adsorption mainly occurred for one day but long-term sorption proceeded for >two weeks. After a one-day or three-week residence time, soil solution was partly replaced (28%). Measurement of concentrations in solution showed rapid desorption, with equilibria being achieved within 1 h (diuron) or a few hours (isoproturon). After 16 successive desorptions done at 30-min or 12-h intervals, equilibration times tended to be longer. For the short residence time, desorption and long-term sorption could occur simultaneously and equilibration might be faster. Residence time had no significant effect on desorption kinetics nor on the small hysteresis observed for diuron. The aging effect, involving long-term sorption only, decreased the proportion of diuron removed from the soil by successive desorptions but, for isoproturon, desorption frequency and desorption kinetics were more important.

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1 INTRODUCTION

Desorption of pesticides from soils involves both kinetic and equilibrium aspects. Kinetics have received little experimental attention. In slurry condition, desorption of four herbicides (monuron, linuron, atrazine and chlorpropham) was shown to be slower than adsorption, with equilibria being achieved over a few days.¹ In contrast, desorption kinetics of cyanazine and metribuzin were rapid and proceeded as fast as adsorption kinetics.² Rapid desorption (<24 h) was also observed for fluroxypyr³ and clomazone.⁴ In practice, when modelling pesticide transfer in soil, adsorption and desorption kinetics are often described using the same equations.^{5,6} Desorption equilibria are usually characterized by desorption isotherms and non-singularity (or hysteresis effect) has frequently been reported. This phenomenon has not yet been totally elucidated. Methodological artifacts⁷ and degradation⁸ have been shown to

be sources of hysteresis, but the possible role of failure to establish complete equilibrium has not been investigated. A two-compartment model has been proposed to describe desorption isotherms, and the existence of molecules strongly adsorbed to soil has been suggested to explain hysteresis.⁹ In addition, modelling sorption kinetics suggests the existence of an irreversibly bound fraction.^{10–12} Experiments using atrazine and metolachlor provide evidence for the existence of labile and resistant sorbed fractions, and the proportion of the resistant fraction (extractable but not desorbed over 24 h) was shown to increase with the age of the residue.¹³ During incubation in soil, changes in the value of the Freundlich desorption coefficient (K_d) of atrazine were time-dependent even after correction for concentration decrease.¹⁴ Pesticide distribution between soil and soil water extract^{3,15} or between soil and soil solution^{16–19} also changed with residence time in soil: this was partly attributed to long-term sorption and

non-linear adsorption isotherms^{3,20} but desorption kinetics and a hysteresis effect might be also involved. Most of these results bring into question the influence of aging on desorption and little is known about this subject.

The aims of this study were thus to (a) determine desorption kinetics of two herbicides (diuron and isoproturon) by undispersed clay loam soil, (b) analyse the role of desorption kinetics on hysteresis, (c) investigate the influence of residence time in soil on desorption and (d) compare adsorption and desorption of the compounds on dispersed (slurry condition) and undispersed soil.

2 MATERIALS AND METHODS

2.1 Soil and chemicals

A sieved (0.5–2 mm) air-dried clay loam soil (sand 18%, silt 49%, clay 33%, organic carbon 1.36%, CEC 20 meq 100 g⁻¹, pH 7.9) collected near Dijon (France) was used in the experiments. Soil moisture content was 5.7% (w/w) on an oven-dry basis and it was determined²¹ to be 62% at 1 kPa.

[*carbonyl*-¹⁴C] Diuron (3-(3,4-dichlorophenyl)-1,1-dimethylurea) and [*carbonyl*-¹⁴C] isoproturon (3-(4-isopropylphenyl)-1,1-dimethylurea) were synthesized as described previously^{19,22} and dissolved in ethanol + water (96 + 4 by volume). The radiolabelled herbicides (99% radiochemical purity) had specific activities of 309 and 337 MBq mmol⁻¹, respectively. Analytical grade compounds (Cluzeau info. labo., Sainte Foy le Grande, France) were dissolved in ethanol + water as above to give a concentration of 2.5 mg litre⁻¹. As required for experimental purposes (see below), different aqueous solutions of radiolabelled herbicides were prepared from the ethanolic solutions.²¹ Ethanol was totally removed but solutions contained sodium azide (200 mg litre⁻¹) as a biocide to prevent degradation of herbicides in soil.²³ Concentration and radioactivity of each solution were checked by HPLC and by liquid scintillation counting.²¹ Radioactivity of solutions was established to supply 5 or 3.3 kBq 10 g⁻¹ equivalent dry soil for diuron or isoproturon, respectively, except where otherwise stated.

2.2 Desorption kinetics studies

Desorption of diuron and isoproturon was triggered either by increasing soil moisture content or by replacing soil solution. In the first method, soil samples (10 g equivalent dry soil) were placed in 5 cm diameter Petri dishes (soil layer was 3–4 mm thick). Known volumes of treatment solutions (2.93 or 5.63 ml at 10.24 or 5.33 mg litre⁻¹, respectively) were applied to the soil surface by pipette. Soil moisture was thus 35 or 62%

and herbicide rate was 3 mg kg⁻¹. Dishes were closed with Parafilm to prevent water evaporation and kept at 18°C. Herbicide concentrations in the soil solution were determined at 1, 3 and 7 days after treatment to evaluate time course changes, as previously described.²¹ Two stacked 42.5 mm diameter glass microfibre filters GF/A (Whatman Ltd, Maidstone, UK) allowed soil solution sampling at the soil surface. The volume and the radioactivity of the liquid phase retained in the upper filter were determined by weighing and by liquid scintillation counting, and herbicide concentration could be calculated. One day after treatment, water (2.7 ml) containing sodium azide (200 mg litre⁻¹) was added to a set of treated soil samples to increase soil moisture from 35 to 62%. Herbicide concentrations in the soil solution were determined at 2, 5, 30 min, 5 h, 1 and 6 days after changing the soil moisture, to evaluate desorption kinetics. Each measurement was done using duplicate samples.

In the second method, soil samples were treated with herbicide solutions (6.44 ml) at 0.94 or 4.66 mg litre⁻¹ (i.e. 0.6 or 3 mg kg⁻¹ soil) to give the same final soil moisture (70%), as described above. After a one-day or three-week residence time in soil at 18°C, one 42.5 mm diameter filter was laid and left at the soil surface for duplicate samples from each condition. Five stacked 42.5 mm diameter filters were then applied for 2 min to each sample to remove soil solution by capillarity. The five moist filters were then placed in a weighed scintillation vial and the volume of soil water retained in the filters (about 2 ml, i.e. 28% of water content) was determined by weighing, taking into account the average weight of the dry filters. Ethanol + water (96 + 4 by volume; 10 ml) was added to the vial and a sample (2 ml) was counted for radioactivity after a 2-h extraction period. The herbicide concentration in the soil solution and the value of the sorption coefficient (mg kg⁻¹/mg litre⁻¹) could be calculated. The removed soil solution was rapidly replaced by an equivalent volume of aqueous solution of sodium azide (200 mg litre⁻¹). Then the solution of each sample was collected using one 25 mm diameter filter applied for 10 s at 5, 30 min, 1, 12 and 24 h after soil solution replacement. The volume (150–200 µl) and the radioactivity of soil solution collected by each filter were determined in a scintillation vial by weighing and by liquid scintillation counting after adding ethanol + water (96 + 4 by volume; 1 ml). Herbicide concentrations in the soil solution and values of the desorption coefficient were calculated taking into account changes in water volumes and in herbicide amounts in soil samples.

2.3 Studies on successive desorption

To study desorption of larger amounts of sorbed diuron or isoproturon, successive desorptions were achieved

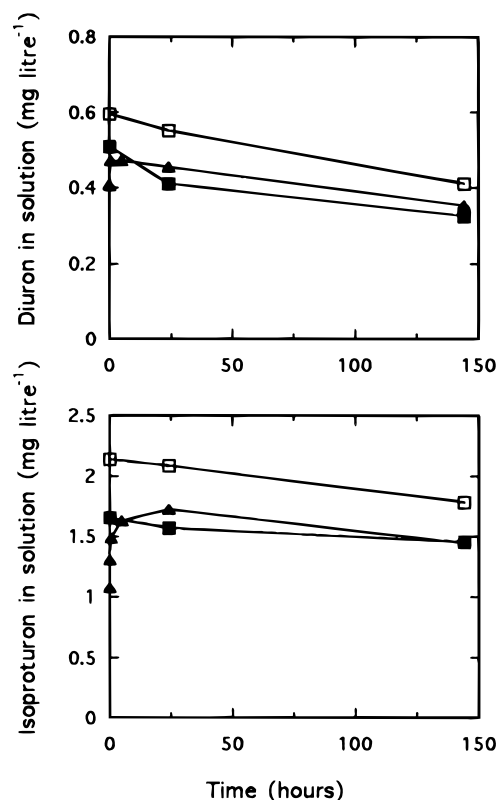


Fig. 1. Changes in herbicide concentrations (mean of two replicates) in soil solution after a 24-h equilibration period for an application rate of 3 mg kg^{-1} . Soil moisture content was kept at (■) 62% or (□) 35%, or (▲) increased from 35 to 62%.

using the replacement method. Soil samples were treated at 0.6 or 3 mg kg^{-1} (70% soil moisture content) and soil solution was replaced after a one-day or three-week (short or long) residence time in soil, as described above. Fifteen additional replacements were carried out at intervals of 30 min or 12 h (fast or slow desorptions). Duplicate samples were used for each condition. At each desorption step, herbicide concentrations in the soil solution were measured and residual amounts of herbicides in samples, sorbed amounts and values of the desorption coefficient were calculated. After the last measurement, the removed soil solution was not replaced but the residual solution of each sample was collected using one 42.5 mm filter at 2 h (diuron, short residence time only), 24, 48, 72 h (isoproturon only) and 96 h (diuron, long residence time only) after the last replacement for the fast desorptions and at 36, 60, 84 h (isoproturon only) and 132 h (diuron only) for the slow desorptions. Herbicide concentrations were determined and values of the desorption coefficient were calculated to assess final desorption kinetics.

2.4 Checking for degradation

To verify that herbicides were not degraded in soil, residual soil samples from successive desorption experi-

ments were exhaustively extracted with methanol. Extracts were concentrated to small volumes and analysed by HPLC.²³

2.5 Influence of soil compaction on desorption kinetics

Although no pressure was applied during successive desorptions, some soil compaction might have occurred and influenced desorption. To evaluate this effect, desorption kinetics were achieved using the replacement method described in Section 2.2 except that pressure (13 kPa) was applied for 2 min to soil samples before starting desorption. In these experiments, diuron and isoproturon were applied at 0.6 mg kg^{-1} and the residence time was one day.

2.6 Long-term sorption measurements

Because sorption equilibria were not achieved over one day and sorption could depend on concentration,²³ changes over time in the adsorption partition coefficient were determined for various herbicide rates. Soil samples were treated with diuron at 0.45 , 0.6 or 3 mg kg^{-1} or isoproturon at 0.24 , 0.6 , 1.2 or 3 mg kg^{-1} , at 70% moisture content. These rates corresponded to initial and final concentrations in the successive desorption experiments. Samples were allowed to equilibrate for one day or three weeks at 18°C , and one 42.5 mm diameter filter was laid and left on the soil surface for duplicate samples from each condition. The solution of each sample was collected using one 25 mm filter applied for 10 s at 0, 4, 8, 24, 72, 144, 216 and 312 h after the one-day equilibration period or at 0, 72, 144, 216 and 312 h after the three-week equilibration period. Herbicide concentrations in solution were measured and values of the sorption coefficient were calculated taking into account changes in water volumes and herbicide amounts in samples.

2.7 Batch experiments

Adsorption and desorption isotherms of diuron and isoproturon by soil were also determined in slurry condition for comparison purpose. Aqueous herbicide solutions were prepared at 0.1 , 0.5 , 1 and 5 mg litre^{-1} and their radioactivity was 113 Bq ml^{-1} for diuron or 70 Bq ml^{-1} for isoproturon. Solutions contained calcium chloride (0.01 M) and sodium azide ($200 \text{ mg litre}^{-1}$) was added with isoproturon only. Adsorption was achieved by mixing 5 g air-dry soil (4.73 g oven-dry soil) and 25 ml solution in 50-ml closed glass flasks with two replicates. Flasks were placed on a horizontal shaker for 24 h. Then they were allowed to settle for 30 min and supernatant phases (20 ml) were centrifuged

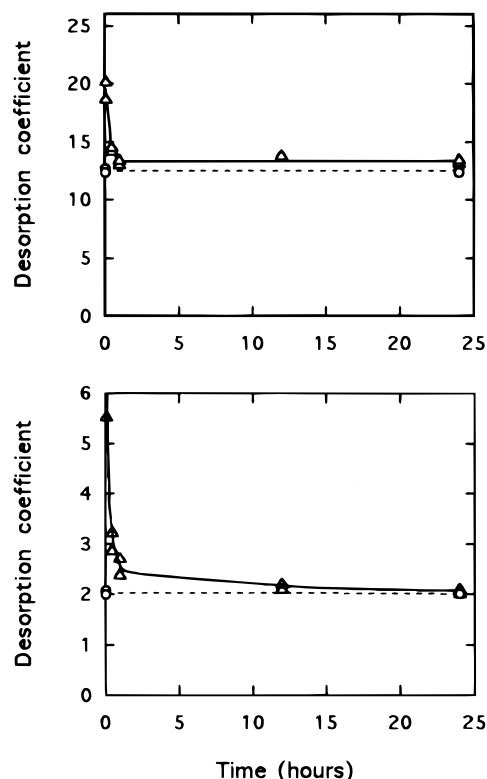


Fig. 2. Desorption kinetics (two replicates) of diuron (top) and isoproturon (bottom) after partial replacement (28%) of soil solution three weeks after treatment at 0.6 mg kg^{-1} . (— Δ —) desorption kinetic, (— \circ —) adsorption control at similar rate and duration.

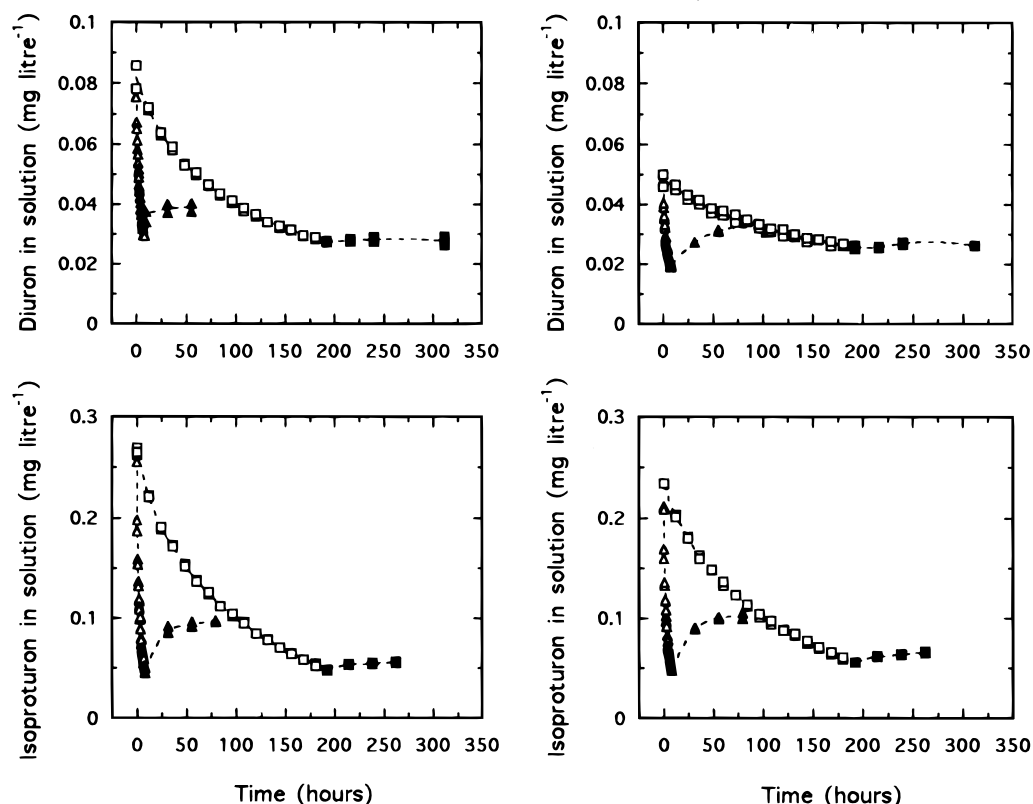


Fig. 3. Changes in diuron or isoproturon concentrations (two replicates) in soil solution (open symbols) during and (closed symbols) after successive desorptions at (Δ , \blacktriangle) 30 min or (\square , \blacksquare) 12 h intervals. Desorption started one day (left) or three weeks (right) after soil treatment at 0.6 mg kg^{-1} .

(10 min, 5500g). A supernatant portion (1 ml) was counted for adsorption measurement. Another portion (18 ml) was removed. The residual pellets corresponding to the 0.1 and 5 mg litre^{-1} concentrations were transferred to the original flasks with 19 ml of fresh solution (without herbicide) for a 24-h desorption period. Herbicide concentrations in solutions were measured and desorption was repeated three-fold as described above.

3 RESULTS

One day after soil treatment at 3 mg kg^{-1} , concentrations of diuron in soil solution were 0.60 and $0.51 \text{ mg litre}^{-1}$ at 35% and 62% soil moisture content, respectively. For isoproturon, the corresponding values were 2.14 and $1.66 \text{ mg litre}^{-1}$ (Fig. 1). Then, for both compounds, concentrations decreased over the following week. When soil moisture was increased from 35 to 62% after a one-day equilibration period, concentrations of diuron or isoproturon in soil water rapidly decreased and 2 min after dilution they were about half of the initial values. Then they increased to the same levels as those in samples kept at 62% soil moisture content, within 30 min for diuron or 5 h for isoproturon.

In soil treated at 0.6 or 3 mg kg^{-1} , at 70% soil moisture content, concentrations of diuron in soil solution

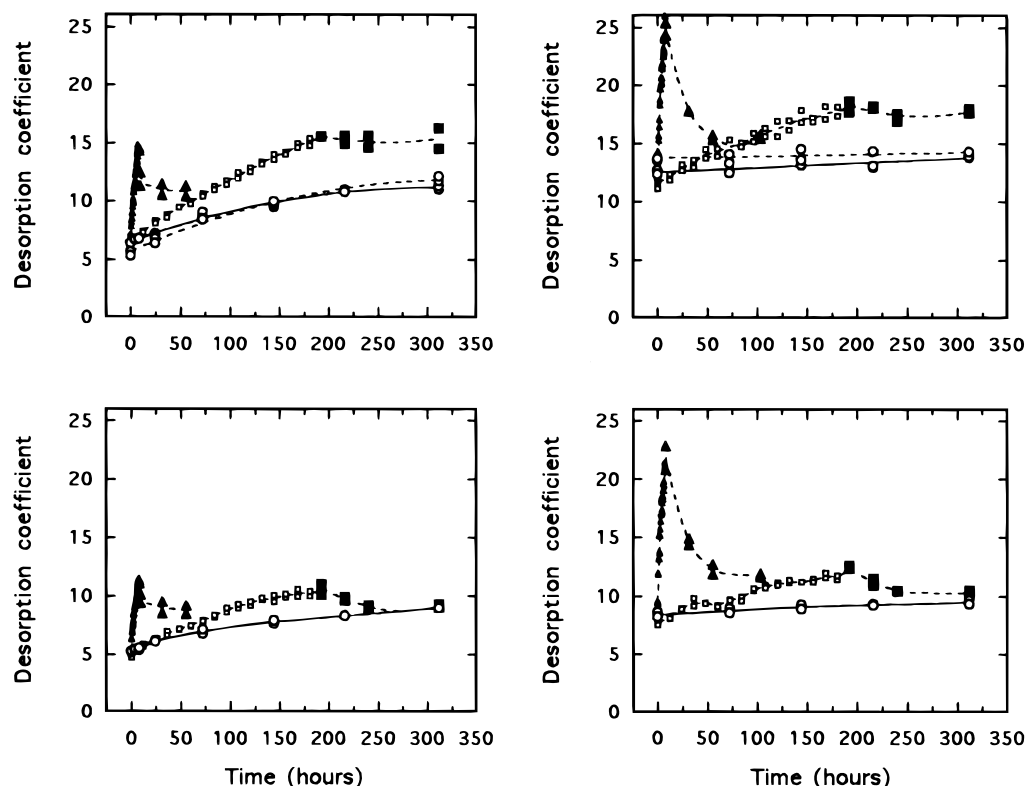


Fig. 4. Changes in values (two replicates) of the desorption coefficient of diuron during and after successive desorptions. Symbols as in Fig. 3. Desorptions started one day (left) or three weeks (right) after soil treatment at 0.6 (top) or 3 mg kg⁻¹ (bottom). Values of the sorption coefficient at rates corresponding to (—○—) initial and (---○---) final concentrations in successive desorption experiments, for the same residence times in soil.

(7 ml) were 0.081 or 0.51 mg litre⁻¹ one day after treatment and 0.046 or 0.31 mg litre⁻¹ three weeks after treatment, respectively. For isoproturon, the corresponding values were 0.26 or 1.55 and 0.21 or 1.34 mg litre⁻¹. The volume of soil solution removed from each sample one day or three weeks after treatment was in the range 1.8–2.2 ml or 1.6–1.9 ml, respectively (data not shown). Larger amounts of isoproturon were thus removed. Because water volumes and total herbicide amounts in samples decreased after each measurement, the desorption coefficient was preferred to describe desorption kinetics and was compared to the sorption coefficient provided by the long-term sorption measurements at similar rate and duration. Results showed the same pattern at both rates and for both residence times before desorption. Accordingly, they are only presented for the low rate and the long residence time (Fig. 2). Values of the desorption coefficient rapidly decreased over 30 min and desorption equilibria were achieved within about 1 h for diuron and less than 12 h for isoproturon. At equilibrium, sorption and desorption coefficients did not differ. Soil compaction had no effect on desorption kinetics (data not shown).

At the end of successive desorptions, the total of the extracted radioactivity and that recovered in filters was usually 98–101% of the applied radioactivity. For diuron, it could occasionally decrease to 96% for the long residence time. Qualitative analysis revealed that

extracts contained a single compound corresponding to the parent molecule (data not shown). Thus, in accordance with previous work,²³ herbicides were not degraded and were fully recovered. Changes in herbicide concentrations in soil solution during and after successive desorptions are presented in Fig. 3. Because results followed the same trend, they are only shown for the low rate. Initial concentrations were similar to those described in kinetic experiments. For diuron, they were higher at the high rate (data not shown), and at each rate they were lower (60–66%) for the long residence time. After the short residence time, concentrations similarly decreased by a factor of 2.5–3 for both fast and slow desorptions. After the long residence time, this decrease was less marked especially for the slow desorptions. Accordingly, at a given rate, differences in final concentrations were small. For isoproturon, initial concentrations were higher at the high rate (data not shown), and for each rate they were slightly lower (84–87%) for the long residence time. Under all conditions, concentrations similarly decreased by a factor of 4–5.

After the last fast desorption, concentrations of diuron increased under any conditions but this increase was less important (30 versus 70%) and equilibrium was achieved more rapidly (about 2 h versus 48 h) for the short residence time (Fig. 3). For isoproturon, concentrations increased by a factor of two and rapid equilibrium was not observed for the short residence time

although some differences in equilibration time occurred (24 versus 48 h) (Fig. 3). After the last slow desorption, concentrations of both herbicides showed little increase (<20%) for a maximum of two days.

Changes in values of the desorption coefficient during and after successive desorptions are shown in Fig. 4 for diuron (both rates) and in Fig. 5 for isoproturon (low rate only). Values of the sorption coefficient determined in long-term sorption measurements at rates corresponding to initial and final concentrations in successive desorptions are also reported for the same

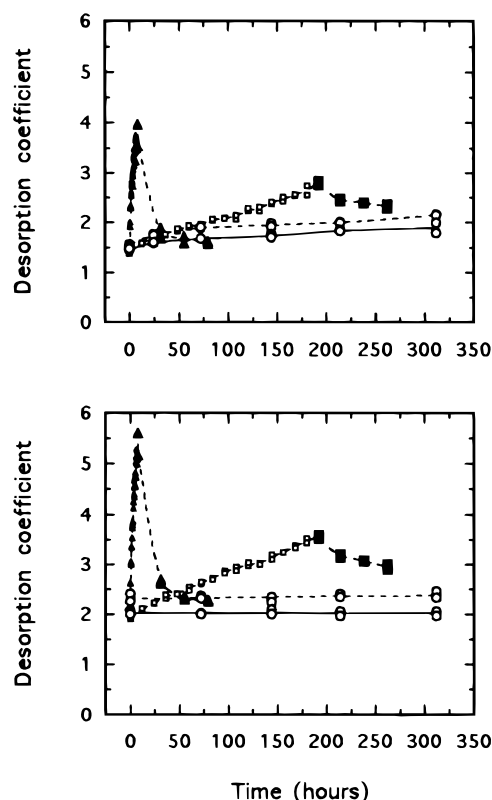


Fig. 5. Changes in values of the desorption coefficient of isoproturon during and after successive desorptions. Symbols as in Fig. 4. Desorptions started one day (top) or three weeks (bottom) after soil treatment at 0.6 mg kg^{-1} . Values of the sorption coefficient as in Fig. 4.

residence times in soil. For both herbicides, values of the sorption coefficient increased as herbicide rate decreased, but the decrease in herbicide concentrations during successive desorptions had little effect. They also increased with residence time in soil especially over the first two weeks. During the fast desorptions, values of the desorption coefficient of diuron increased by a factor of 2.5 under all conditions (Fig. 4). During the slow desorptions, a similar increase was observed for the short residence time, whereas it was less important for the long residence time. Values always increased more rapidly than those of the sorption coefficient. Differences were higher at the low dose but they did not appear to be influenced by residence time. A similar pattern was observed for isoproturon except that increase in values of the desorption coefficient was always less important for the slow desorptions and under this condition there were little differences between sorption and desorption coefficients (Fig. 5).

After the last desorption, values of the desorption coefficient decreased (Figs 4 and 5). At equilibrium, figures were close to those of the sorption coefficient at the corresponding rates except for the slow desorptions of diuron at the low dose showing similar hysteresis for both residence times. Under these conditions, (Table 1) there was no significant difference (ANOVA; $cv = 0.7\%$)²⁴ between the amounts adsorbed by soil (estimated from the sorption coefficient), but a significant difference ($cv = 1.7\%$) in the concentrations in soil solution. This hysteresis appeared to be due to tiny amounts of undesorbed herbicide.

Under all conditions, amounts (expressed as percentage of applied) of sorbed and residual (total soil/water system) herbicides decreased simultaneously during successive desorptions, and the amount of dissolved herbicide was reduced (data not shown). Diuron was mainly adsorbed on soil (6–13% was initially found in soil solution). From 15 to 33% of the applied herbicide could be removed: statistical analysis (ANOVA) showed that, regardless of the significant interactions, average amounts were significantly lower for the long residence time (19.3 versus 27.7%), the low dose (20.6 versus

TABLE 1
Comparison of Diuron Distribution in Soil and in Soil Solution after the Slow Desorptions and after Sorption under Similar Conditions (Rate and Duration)^a

Residence time (days)	Residual amount ^b (μg)	Solution (mg litre^{-1}) ^b		Adsorbed (mg kg^{-1}) ^b	
		Ads ^c	Des. ^c	Ads.	Des.
1	4.385	0.0372	0.0283	0.422	0.426
21	4.770	0.0326	0.0270	0.462	0.465

^a Diuron was applied at the low rate (0.6 mg kg^{-1}) and the equilibration was allowed for one day or three weeks before desorptions.

^b Mean of two replicates.

^c Ads.: adsorption; Des.: desorption.

26.4%) and the fast desorption (21.2 versus 25.8%) ($cv = 3.6\%$). A similar pattern was observed for amounts of diuron released from the sorbed fraction (12.2–28.7%). Isoproturon was less adsorbed on soil (26–37% was initially found in soil solution). From 50 to 75% of the applied herbicide could be removed; average amounts were significantly lower for the fast desorptions (56.4 versus 68.1%), the long residence time (60.6 versus 67.6%) and the low dose (60.2 versus 64.2%) ($cv = 2.5\%$). Amounts of isoproturon released from the sorbed fraction (35.7 to 68.9%) showed the same pattern.

Under slurry conditions, Freundlich adsorption isotherms showed that diuron was more adsorbed than isoproturon (Fig. 6). Desorption isotherms showed no hysteresis for isoproturon and a small hysteresis effect for diuron at low concentrations. Freundlich adsorption isotherms of herbicides on the undispersed soil were also determined from the long-term sorption measurements after one-day and three-week equilibration periods and compared to those obtained under slurry conditions for the same concentration range (Fig. 7). Adsorption of diuron on the dispersed soil was higher ($K_f = 6.0$, $1/n = 0.88$) than adsorption on the undis-

persed soil after the short residence time ($K_f = 4.93$, $1/n = 0.9$) but lower than that on the undispersed soil after the long residence time ($K_f = 7.17$, $1/n = 0.83$). Isoproturon was similarly adsorbed on dispersed and undispersed soil after one-day equilibration time ($K_f = 1.3$, $1/n = 0.9$) but was more adsorbed on undispersed soil after three weeks ($K_f = 1.59$, $1/n = 0.86$).

4 DISCUSSION

Diuron was more adsorbed on the undispersed soil than isoproturon and, for both herbicides, adsorption increased with decreasing rate. Adsorption mainly occurred over the first day but further decrease in herbicide concentrations in soil solution (and thus increase in values of the sorption coefficient) proved that sorption proceeded for more than two weeks, since the herbicides were not degraded. This long-term sorption might be attributed to diffusion into organic matter and/or small pores^{25,26} and has been shown to involve a few percent of the applied compounds.²³

Under all conditions, the first desorption step was rapid since it was achieved within 1 h (diuron) or a few hours (isoproturon). Short-term adsorption has been shown to proceed similarly.²¹ However, it should be noted that desorption of diuron involved only a small fraction of the adsorbed herbicide and the slower desorption of isoproturon might be related to the larger amounts desorbed. Desorption did not depend on residence time in soil as previously observed for clomazone.⁴

Because equilibria could require longer time (one day or more) after the last desorption and no compaction effect could be involved, it is thought that desorption became slower and slower as it proceeded (especially for diuron). However, that would be limited since, for both herbicides, equilibria were nearly achieved during the slow (12 h) desorptions. It is worth noting the lower increase in diuron concentrations in soil solution and the faster equilibrium attainment observed after the fast desorptions for the short residence time. Under this condition, desorption of rapidly adsorbed diuron and long-term sorption might occur simultaneously and thus apparent equilibria would be more rapidly achieved. Moreover, because the rapid initial (2 h) increase in concentrations was not observed for the long residence time, it is thought that longer residence time in soil might favour the decrease in speed of attainment of desorption equilibria as desorption proceeds but that would be also limited since no residence time effect was observed for the slow desorptions. Isoproturon appeared to follow the same trend but none of the phenomena was as clear as for diuron. That would be partly due to lower long-term sorption of the herbicide. Accordingly, for the system studied, desorption kinetics are expected to have no impact on degradation, which usually occurs at slow rate, but are likely to influence

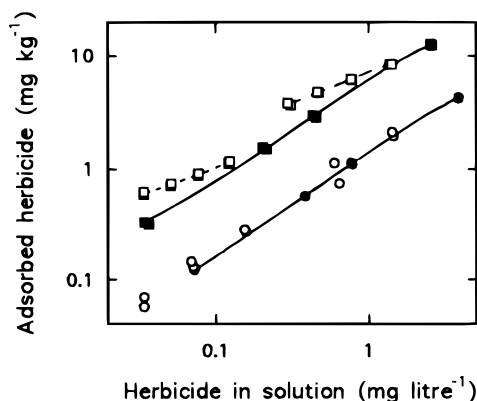


Fig. 6. (■, ●) Adsorption and (□, ○) desorption isotherms of (■, □) diuron and (●, ○) isoproturon on soil in slurry condition.

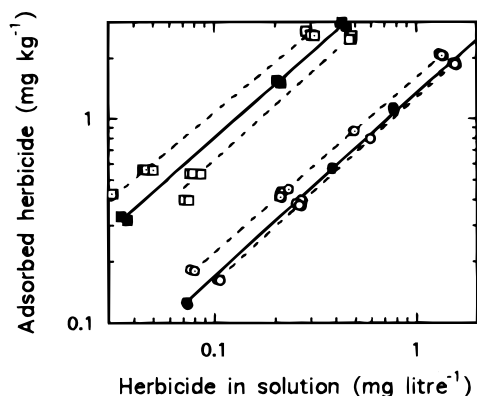


Fig. 7. Adsorption isotherms of (■, □, □) diuron and (●, ○, ○) isoproturon on (■, ●) dispersed soil (one day slurry condition) or undispersed soil after (□, ○) one day or (□, ○) three weeks.

mobility in soil.

Despite the large amounts desorbed, desorption of isoproturon showed no hysteresis. Accordingly, this phenomenon could not be involved in the increase in value of the partition coefficient between soil and soil solution observed during degradation in previous work.^{19,20} Some hysteresis was detected for diuron, mainly at the low rate as already emphasized.¹² However, a comprehensive study would require further desorption of diuron and this aim cannot be easily achieved using filters because of the low replacement rate of soil solution. Under our experimental conditions, residence time in soil did not influence hysteresis. Accordingly this factor appeared to have little effect on herbicide desorption (kinetic and hysteresis). However, it may be noticed that soil microflora were controlled by sodium azide and thus results might be different in soil with normal biological activity. It would be also interesting to investigate the influence of residence time on desorption for other soil types with higher organic matter content.

During successive desorptions, values of the desorption coefficient substantially increased. For the fast desorptions, this increase mainly resulted from the lack of desorption equilibrium. Because water replacement corresponded to a low rainfall intensity (about 2 mm h^{-1}), increase should be more important for heavy rainfall. For the slow desorptions, the role of non-equilibrium was reduced but long-term sorption (for the short residence time) and hysteresis (for diuron) were involved. As compared to diuron, higher proportions of isoproturon were removed from the soil/water system in relation to lower adsorption of this herbicide. For both compounds proportions were smaller as the application rate decreased and as residence time or desorption frequency increased. For the more strongly sorbed diuron, residence time was the most important factor and its effect mainly relied on long-term sorption. For the less adsorbed isoproturon, desorption frequency was more important, and desorption kinetics, requiring longer equilibration time, played a major role.

Over a one-day equilibration period, diuron was more adsorbed on dispersed soil (slurry condition) than on undispersed soil. That might be due to better diffusion of diuron into soil aggregates and to the lack of sodium azide capable of decreasing adsorption.²³ Such a difference was not observed for isoproturon for which sodium azide was added in both dispersed and undispersed conditions. However, for both herbicides, the 24-h slurry condition would not allow complete equilibration since adsorption on undispersed soil was higher after three weeks. A similar conclusion has been drawn for alachlor.¹⁰ Accordingly batch measurement over a one-day period may provide a realistic estimation of adsorption for a short residence time in soil but will underestimate adsorption for a long residence time in soil.

4 CONCLUSIONS

Adsorption of diuron and isoproturon on the studied clay loam soil mainly occurs over the first day but significant long-term sorption proceeds for more than two weeks. Dilution or partial replacement of soil water causes rapid desorption, and equilibrium is achieved within 1 h (diuron) or a few hours (isoproturon). After successive desorptions, equilibration times tend to be longer. However, for short residence times in soil, desorption and long-term sorption may occur simultaneously and apparent equilibrium may be rapidly achieved. Residence time in soil appears to have no significant effect on desorption kinetics nor on the small hysteresis effect observed for diuron desorption. Thus, under our experimental conditions, the aging effect would involve long-term sorption only. This phenomenon is mainly responsible for reducing the proportions of diuron removed from soil by successive desorptions but for isoproturon the roles of desorption frequency and desorption kinetics are more important. A 24-h adsorption in slurry condition may be similar to short-term adsorption on undispersed soil but it provides underestimation of long-term sorption.

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